High Strength Aluminum Alloys and Process for Making the Same

Cross Reference to Related Applications

[0001] This application claims the benefit, under 35 U.S.C. 119(e), of U.S. Provisional Application No. 60/464,654, which was filed on April 23, 2003.

Background Of The Invention

1. Field of the Invention

[0002] The present invention relates, in general, to a high strength aluminum alloy based on the Al-Zn-Mg-Cu alloy system and a process for forming the same. Although not limited thereto, the alloys are particularly suited for use in sporting goods and aerospace applications.

2. Description of the Background Art

[0003] The highest strength aluminum alloys known at this time are based on the aluminum-zinc-magnesium-copper system. Commercial high-strength alloys currently being produced include AA7055 (nominally 8% Zn-2% Mg-2.2% Cu-0.10% Zr), AA7068 (nominally 7.8% Zn-2.5% Mg-2.0% Cu-0.10% Zr) and a Kaiser Aluminum alloy designated K749 (nominally 8% Zn-2.2% Mg-1.8% Cu-0.14% Zr). These alloys are shown graphically on the equilibrium diagram in FIG. 1, which depicts the published phase relationships at 860°F for an alloy containing 8% Zn. As may be seen, K749 is near a phase boundary, while the other two alloys are in multiple phase fields. In the latter case all the alloying elements are not in solid solution at 860°F, and are not only unavailable for age hardening, but the undissolved phases remaining after heat treatment detract from toughness. Although solution heat treating at a higher temperature than 860°F will dissolve more of the solute, care has to be taken to ensure that the alloy does not undergo eutectic melting, which is a common problem in commercially cast alloys that have locally enriched regions as a result of microsegregation that occurred during casting.

[0004] There is a need in many applications, such as sporting goods and aerospace applications, for even stronger alloys based on the aluminum-zinc-magnesium-copper system that do not sacrifice toughness. However, this requirement presents a problem because, in general, as the tensile strength of an aluminum alloy is increased, its toughness decreases.

Summary of the Invention

[0005] The present invention addresses the foregoing need in a number of ways. More particularly, there are three distinct avenues for increasing an alloy's strength while maintaining its toughness: rich alloy chemistries; processing to maximize alloying effectiveness; and preventing recrystallization. Rich alloys provide more solute, which is

potentially available for age hardening to higher strength levels; effective processing ensures that the solute is available for strengthening and not out of solution as second phases, which detract from fracture toughness; and maintaining an unrecrystallized microstructure optimizes both strength and toughness.

[0006] To provide increased tensile strength without sacrificing toughness through the use of rich chemistries, the present invention comprises aluminum alloys based on the Al-Zn-Mg-Cu alloy system that preferably include high levels of zinc and copper. In addition, small amounts of scandium are also preferably employed to prevent recrystallization. Each of the alloys preferably includes at least 8.5% Zn and 1.8% Cu by weight. Higher levels of each of these elements up to about 11.0% Zn and 2.6% Cu can be used. The preferred ranges of all elements in the alloys include by weight, 8.5-11.0% Zn, 1.8-2.4 % Mg, 1.8-2.6% Cu, and at least one element from the group Zr, V, or Hf not exceeding about 0.5%, the balance substantially aluminum and incidental impurities. In the preferred embodiments, 0.05-0.30% Sc is also included in the alloys to prevent recrystallization.

[0007] To maximize alloying effectiveness during formation of the alloys, a homogenization process is preferably employed after alloy ingot casting in which a slow rate of temperature increase is employed as the alloy is heated as near as possible to its melting temperature. In particular, for the last 20-30°F below the melting temperature, the rate of increase is limited to 20°F/hr. or less to minimize the amount of low melting point eutectic phases and thereby further enhance fracture toughness of the alloy.

[0008] The foregoing alloys and processing operations enhance the properties of the Al-Zn-Mg-Cu alloy system, such that they can be more effectively employed in numerous applications. Specific products or items in which the subject alloys can be employed include, among others, sporting goods including baseball and soft ball bats, golf shafts, lacrosse sticks, tennis rackets, and arrows; and aerospace application including aerospace components such as wing plates, bulkheads, fuselage stringers, and structural extrusions and forgings; and ordnance parts such as sabots and missile launchers.

Brief Description of the Drawings

[0009] The features and advantages of the present invention will become apparent form the following detailed description of a preferred embodiment thereof, taken in conjunction with the accompanying drawings, in which:

[0010] FIG. 1 is an equilibrium diagram which depicts the published phase relationships at 860°F as a function of percentages of Cu and Mg for three known alloys each containing about 8% Zn;

[0011] FIG. 2 is an equilibrium diagram which depicts the phase relationships at 860°F as a function of percentages of Cu and Mg for two alloys formed in accordance with the preferred embodiments and compared with a third known alloy containing about 8% Zn;

[0012] FIG. 3 is a graph depicting fracture toughness as a function of the average (of longitudinal and transverse) yield strength for a number of sample alloys;

[0013] FIG. 4 is a graph illustrating the effect on yield strength of adding scandium to an alloy that has been extruded in a first case and formed into a sheet in a second case;

[0014] FIG. 5 is a graph depicting second phase volume percent as a function of heating rate in a formation process for Alloy AA7068;

[0015] FIG. 6 is an equilibrium diagram which depicts the phase relationships at 860°F as a function of percentages of Cu and Mg for two alloys formed in accordance with the preferred embodiments; one with 9% Zn and the other with 10% Zn;

[0016] FIG. 7 is a graph illustrating the effect of magnesium and copper on strength of Al-Zn-Mg-Cu alloys; and

[0017] FIG. 8 is a graph illustrating the effect of zinc on strength of Al-Zn-Mg-Cu alloys.

Detailed Description of the Preferred Embodiments

[0018] The following examples illustrate how alloy modifications and efficient processing operations can be used to enhance the properties of the Al-Zn-Mg-Cu alloy system in accordance with the preferred embodiments of the present invention, such that they can be more effectively utilized in sporting goods and aerospace applications.

Example 1

[0019] The alloy compositions listed in Table 1 were cast as 9" billet, most of which contained a relatively high nominal zinc content of 9%.

TABLE 1

		% by wt. (Spectrographic analysis)					
Alloy No.	Si	Fe	Cu	Mg	Zn	Zr	Sc
45	0.02	0.04	1.41	2.57	7.96	0.12	0.053
36	0.03	0.06	1.91	2.17	9.02	0.15	0.054
39	0.04	0.05	1.28	2.74	9.02	0.13	0.059
43	0.03	0.03	1.44	2.55	9.04	0.13	0.053
47	0.04	0.06	1.59	2.34	8.95	0.14	0.055

[0020] These alloys are depicted on the 860F (F= degrees Fahrenheit) phase diagram in FIG. 2 together with a K749 "control" containing nominally 8% Zn. Note that all of these alloys contain about .05% scandium, an element which in combination with zirconium is effective in preventing recrystallization.

[0021] The billets were homogenized at 880°F and extruded to seamless tubes 4" in diameter with a 0.305" wall thickness. After sections of the extrusions were cut and flattened to pieces about 12" square, they were solution heat treated at 880°F and quenched in cold water. They were then tested for tensile properties and fracture toughness in a peak-aged condition, the results of which are provided in Table 2.

TABLE 2

Alloy No.	Cu	Mg	Zn	Yield Strength (ksi) Long.	Yield Strength (ksi) Trans.	Kpmax (ksi rt.in.)
K749	1.98	2.18	8.02	91.5	92.4	28.6
36	1.91	2.17	9.02	94.9	94.6	24.5
39	1.28	2.74	9.02	92.7	94.6	20.2
45	1.41	2.57	7.96	91.1	89.9	26.1
43	1.44	2.55	9.04	93.9	94.9	21.3
47	1.59	2.34	8.95	93.9	95.2	22.7

[0022] The effect of raising the zinc from 8% to 9% can be seen by comparing alloys K749 with #36 (at nominally 2.2% Mg - 2% Cu) and alloy #45 with #43 (at nominally 2.6% Mg - 1.4% Cu). The average increase in yield strength is about 3.5 ksi. The observed decrease in toughness is what would be expected in accordance with the strength increment, i.e., approximately 1 ksi rt.in. per ksi in yield strength; however, the high Mg - low Cu alloys have a poorer combination of strength and toughness than the more balanced K749-type composition. This is shown graphically in FIG. 3, where fracture toughness is plotted against the average (of longitudinal and transverse) yield strength.

Example 2

[0023] Another alloy similar to #36, except for a 0.11% Sc content (9.22% Zn - 2.14% Mg - 1.88% Cu) was prepared and likewise extruded to a 4" diameter tube with a

0.305" wall thickness. Tubes of this alloy together with K749 and #36 (both with 0.05% Sc) were subsequently cold drawn to a diameter of 2.25" and a 0.10" wall thickness. After solution heat treating and aging, longitudinal yield strengths were measured with the results in Table 3.

TABLE 3

Alloy	Cu	Mg	Zn	Sc	Yield Strength (ksi)
K749	1.98	2.18	8.02	0.050	99.3
36	1.91	2.17	9.02	0.054	103.3
37	1.88	2.14	9.22	0.107	104.0

[0024] Note that the experimental alloys with the higher zinc concentrations again were significantly stronger than the K749 alloy with 8% Zn. Also, noteworthy is the fact that both alloys containing 0.05% Sc maintained much higher strength levels after the cold drawing operation than was evident in the as-extruded condition (compare with previous table). In other words, as little as 0.05% Sc was sufficient to prevent recrystallization during the solution heat treating operation. As will be discussed in the next example, this is important from an economic viewpoint, because scandium is extremely rare and very expensive.

<u>Example 3</u>

[0025] It has been recognized for a number of years that scandium in combination with zirconium is an effective recrystallization inhibitor. A Russian review article noted that it is desirable to add scandium to aluminum alloys in a quantity from 0.1 to 0.3% together with zirconium (0.05-0.15%). However, the greatest effect is observed for alloys not containing alloy elements combining with scandium in insoluble phases; with a limited copper content [scandium combines with copper] alloying with scandium together with zirconium of Al-Zn-Mg-Cu and Al-Cu-Li alloys is possible. As such, commercial alloys based on Al-Zn-Mg-Sc-Zr have been developed.

[0026] Two potential drawbacks to scandium additions to 7XXX alloys containing about 2% copper are evident:

[0027] 1) the copper level is high enough to combine with scandium, thereby rendering it ineffective, and

[0028] 2) the high price of scandium; at the 0.2% level it would add about $10 a pound to the cost of the aluminum alloy.

[0029] It would therefore be economically and technically attractive if scandium levels could be effectively used below those recommended in the Russian literature.

[0030] Alloys of the compositions listed in the following table were prepared as 5" diameter billets, which were processed as described below in Table 4.

TABLE 4

Alloy No.	% by wt.						
	Si	Fe	Cu	Mg	Zn	Zr	Sc
A	0.03	0.04	1.95	2.20	8.07	0.11	0.00
B	0.03	0.05	1.86	2.17	8.05	0.00	0.22
C	0.03	0.05	1.89	2.18	8.09	0.11	0.06
D	0.03	0.04	1.84	2.12	8.11	0.12	0.11
E	0.03	0.05	1.95	2.18	8.08	0.11	0.22

[0031] The ingots were homogenized at 875°F using a 50°F/hr heating rate and air cool, and then reheated to 800°F and extruded to a 0.25" by 3" flat bar. Sections of each extrusion were annealed at 775°F for 3 hr, cooled 50°F/hr to 450°F, held 4 hr and cooled 50°F/hr to room temperature. The sections were then cold rolled to 0.040" sheet using five pass reductions (84% total reduction). The sheets were solution heat treated at 885°F for 30 min, quenched in cold water, and then aged to the peak strength condition (10 hrs. at 305°F). The as-extruded bars were also heat treated similarly and both products were tested for transverse tensile properties, as listed in Table 5. The specific effects of scandium on strength are also shown in FIG. 4.

TABLE 5

Alloy No.	%Zr	%Sc	UTS (ksi)		Yield Strength (ksi)	
			Extrusion	Sheet	Extrusion	Sheet
A	0.11	0	94.7	90.7	91.4	87.8
B	0	0.22	88.2	92.0	86.1	88.4
C	0.11	0.06	95.7	97.1	92.2	93.3
D	0.12	0.11	95.2	96.6	92.2	93.3
E	0.11	0.22	94.5	96.5	91.1	92.5

[0032] A number of points are evident from these results:

[0033] 1) The strongest alloy in both extrusion and sheet form contains 0.06% Sc (with 0.11% Zr).

[0034] 2) At the 0.1% Zr level, 0.06% Sc is effective in raising the strength of the sheet product by about 6 ksi.

[0035] 3) 0.22% Sc in the absence of zirconium raises the strength of the sheet product by only 1 ksi, and lowers the extrusion strength by about 6 ksi. The effectiveness of only 0.06% Sc in preventing recrystallization was confirmed by comparing the microstructures of the sheet products containing (a) 0.11% Zr, (b) 0.11% Zr + 0.06% Sc, and (c) 0.22% Sc (no Zr) .

[0036] In view of the foregoing, the preferred range in the alloys for Sc is 0.05-0.30%, with a more preferred range of 0.05-0.10% and a most preferred value of 0.06%.

Example 4

[0037] As noted earlier it is important that undissolved second phases not remain after processing so that fracture toughness can be maximized. To illustrate how homogenizing practice can affect the amount of such undissolved phase(s), samples of as-cast AA7068 alloy billet were heated from 850°F at various rates in a differential scanning calorimeter (DSC), and the energy associated with eutectic melting, which started at about 885°F was measured. This energy measurement is directly proportional to the amount of undissolved second phase remaining at the incipient melting point, and the relationship between these factors has been determined by quantitative microscopy. As was shown in FIG. 1, the relatively rich 7068 alloy is well within a multiple phase field at 860°F, and would be expected to have a

significant amount of undissolved second phase unless processed very effectively. FIG. 5 shows how heating rate affects the amount of this phase as determined from the DSC data.

[0038] Note that a slow heating rate of about 10°F/hr reduces the amount of second phase (probably "S" and "M") to a level below 1 vol.%. One would expect that a ~5°F/hr heating rate would reduce the "soluble" portion to near zero. We note that for heating rates of 10-20°F/hr, the volume fraction of undissolved eutectic is no greater than the amount of insoluble Fe-containing constituent (independent of heating rate or homogenization temperature) at a nominal 0.12% Fe level (approx. 1 vol.%).

<u>Example 5</u>

[0039] A series of alloys containing either nominally 9% or 10% zinc (see Table 6) were cast as 6" diameter billets. Copper and magnesium concentrations ranged from 2.0% to 2.5% and 2.0 to 2.4%, respectively, such that a nominal Mg/Cu ratio of 1.0 was maintained. These compositions are shown diagrammatically in FIG. 6 relative to the 860°F equilibrium diagram for 8% zinc.

TABLE 6

			% by wt.			
Alloy No.	Si	Fe	Cu	Mg	Zn	Zr
84	0.03	0.07	1.88	1.96	9.84	0.10
88	0.04	0.07	2.12	2.08	8.52	0.10
86	0.06	0.08	2.34	2.42	8.58	0.10
94	0.07	0.09	2.00	2.14	10.04	0.10
95	0.07	0.08	2.30	2.36	10.18	0.11
99	0.08	0.08	2.46	2.50	10.00	0.10

[0040] The billets were homogenized for 8 hr at 870°F plus 12 hr at 885-890°F using a 10° F/hr heating rate from 870°F. This heating rate was chosen based on FIG. 5, which showed that a slow heating rate of 5-20°F/hr is desired to minimize the amount of undissolved second phase in the alloy that would detract from good mechanical properties, particularly fracture toughness. This slow heating rate should preferably be employed from 20-30 degrees below the alloy melting temperature, up to the homogenization temperature,

which is chosen to be as close to the melting temperature, e.g., within about 5°F, as possible. The homogenized billets were then extruded to a 0.75" by 2.5" bar section, which was solution heat-treated at 885°F. The resultant T6 tensile properties obtained by artificial aging at 250°F for 24 hours are listed in Table 7 and are shown graphically in FIG. 7, where yield strength is plotted against magnesium plus copper content.

TABLE 7

Alloy No.	UTS (ksi)	YS (ksi)	% Elgn
84	100.7	97.1	16.3
88	103.0	99.0	15.5
86	105.0	100.6	15.0
94	103.5	100.6	15.5
95	106.9	103.9	13.5
99	106.9	103.7	11.8

[0041] This graph shows that strength increases up to a concentration of about 4.7% total magnesium plus copper. Since it is known that magnesium levels above about 2.2% result in decreased toughness in Al-Zn-Mg-Cu alloys, it is desirable to maintain the copper at a level of about 2.2% or more to obtain the maximum strength benefit.

[0042] Additional experiments were conducted to evaluate the effect that different levels of zinc have on yield strength in Al-Zn-Mg-Cu alloys. Four different allows were evaluated as listed in Table 8. The results are graphically depicted in FIG. 8 which show that the yield strength of the Al-Zn-Mg-Cu alloys increases almost linearly in the range of between 8.6% and 10.1% Zn.

TABLE 8

Alloy #	Si %	Fe %	Cu %	Mg %	Zn %	Ti %	Zr %	Sc %
0189	0.04	0.08	2.14	1.89	8.60	0.012	0.12	0.05
0190	0.03	0.09	2.31	1.86	9.21	0.016	0.13	0.05
0191	0.03	0.11	2.35	1.81	9.63	0.019	0.13	0.05
0192	0.04	0.10	2.33	1.87	10.13	0.015	0.12	0.05

[0043] Although the present invention has been described in terms of a number of preferred embodiments and variations thereon, it will be understood that numerous additional variations and modifications may be made without departing from the scope of the invention. Thus, it is to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described above.